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Catalytic growth of single-wall carbon nanotubes from metal particles

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Abstract

Single-walled carbon nanotubes (SWNTs) have been synthesized at milligram per hour rates by the catalytic decomposition of both carbon monoxide and ethylene over a supported metal catalyst known to produce larger multiwalled nanotubes. Under certain conditions, there is no termination of nanotube growth, and production appears to be limited only by the diffusion of reactant gas through the product nanotube mat that covers the catalyst. Further development of the catalyst geometry to overcome the diffusion limitation may allow bulk catalytic production of SWNTs by supported metal catalysts. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Single-wall carbon nanotubes (SWNTs) have been previously produced in high yield by laser vaporization of a graphite rod doped with Co and Ni [1]. These high-quality samples have for the first time enabled experimental confirmation of the structurally dependent properties predicted for carbon nanotubes [2,3]. High-quality SWNTs have also been generated by arc evaporation of a graphite rod doped with Y and Ni [4]. These techniques allow production of only gram quantities of SWNTs. Another way to synthesize nanotubes is by catalytic decomposition of a carbon-containing gas by nanometer-scale metal particles supported on a substrate. The carbon feedstock molecules decompose on the particle surface, and the resulting carbon atoms then diffuse through the particle and precipitate as a part of nanotube from one side of the particle. This procedure typically produces imperfect multiwalled nanotubes in high yield [5]. Its advantage is that it is relatively simple and can be scaled to produce nanotubes by the kilogram [6]. Clearly, a method of making high-quality SWNTs by catalytic decomposition could lead to economic production of SWNTs in bulk.

There are two reports of SWNTs produced by catalytic decomposition of stable gas-phase carbon-containing molecules on pre-formed catalytic particles. Peigney et al. reported a mixture of single- and multiwalled nanotubes resulting from decomposition of CH_4 at 1050°C on an alumina-supported Fe cata-

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lyst [7]. They do not report the relative amounts of single- and multiwalled nanotubes. Dai et al. reported the growth of SWNT and a small amount of double-wall nanotubes (DWNTs) by disproportionation of CO on alumina-supported Mo particles at 1200°C [8]. The nanotubes had diameters ranging from 1 to 5 nm and were 100 nm to microns in length, but grew in low yield and appeared by transmission electron microscopy (TEM) observation to be more defective than SWNT formed by the laser vaporization or arc techniques.

We report here the production of high-quality SWNTs, in some cases including DWNT, in yields much larger than previously reported by catalytic decomposition of carbon-containing precursor gases. Under certain conditions, it appears that SWNTs can grow continuously to arbitrary length. Our results demonstrate a means for nucleating and growing nanotubes only from the smallest of the supported catalyst particles, which produce SWNTs, while deactivating the larger particles so that no multiwalled

nanotubes are produced. This allows the growth exclusively of SWNTs from catalyst systems previously thought to produce only larger-diameter multiwalled nanotubes.

2. Experimental

SWNTs are grown by passing carbon-containing gases (CO or C_2H_4) at elevated temperatures over nanometer-size metal particles supported on larger (10–20 nm) alumina particles. Two different metal catalysts have been used, one containing pure Mo, the other containing Fe and Mo in a ratio of 9:1. Both catalysts are made using a method described previously [5]. Briefly, fumed alumina (Degussa) is stirred with methanol, and to the resulting slurry is added a methanol solution of metal salts (ferric nitrate and/or bis(acetylacetonato)-dioxomolybdenum(VI)). The combined slurry is stirred for several hours, dried in a rotary evaporator, baked in
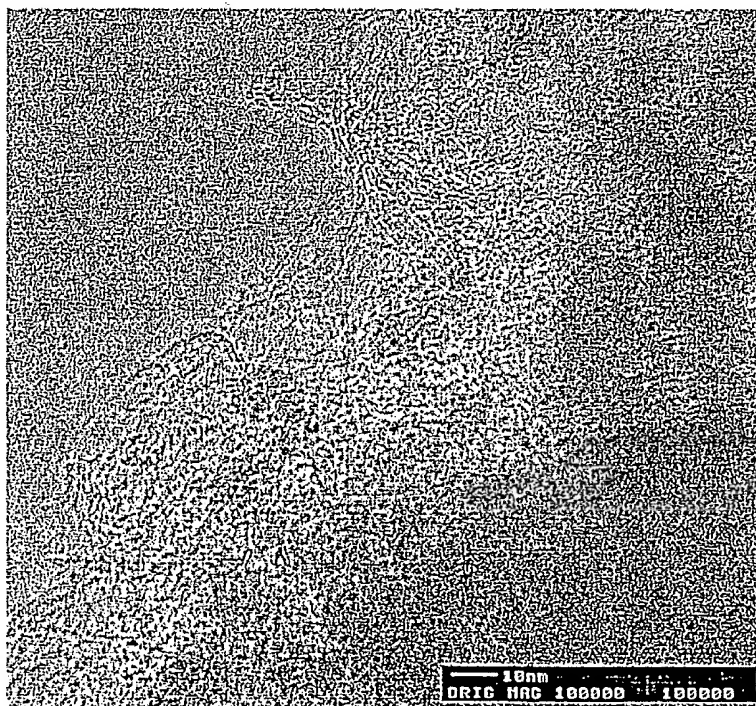

Fig. 1. Individual SWNT grown by reacting 1200 sccm CO at 850°C over an alumina-supported Mo particle system.

vacuum at 180°C for 12–15 h, and ground into a fine powder.

For each growth experiment, a quartz boat containing a carefully weighed amount (typically 20 mg) of the catalyst powder was placed in the center of a 1 inch quartz tube furnace. The system was purged with Ar, then heated under flowing reactant gases to an elevated temperature for a controlled time. The resulting catalyst material, which now also contains reaction products dominated by SWNTs, was removed from the boat and weighed again. The yield is defined as the mass increase divided by the original catalyst mass. Samples were prepared for TEM imaging by sonicating this material in methanol and drop-drying the resulting suspension onto TEM grids.

3. Results

The production of SWNTs by the disproportionation of CO over alumina-supported Mo particles has been greatly improved since an initial report by this laboratory [8]. The catalyst is 34:1 alumina:Mo by mass. The reaction is carried out at 850°C under a flow of 1200 sccm of CO at 900 Torr. The resulting material, which consists of SWNT very monodisperse in diameter (0.8–0.9 nm), is shown in Fig. 1. Particles of the fumed alumina support, 10–20 nm in size, are also visible in this and subsequent TEM images. The yield of nanotubes is plotted as a function of reaction time in Fig. 2. Note that yield continues to increase even for very long reaction times.

CO also forms nanotubes with a second catalyst, this one prepared with 90:9:1 alumina:Fe:Mo by mass. The reaction, when carried out exactly as described above for the alumina:Mo catalyst, yields nanotubes of a wider diameter distribution, 0.5–3 nm, with SWNTs and some DWNTs. A representative TEM image is shown in Fig. 3. For this catalyst, the yield increases with time initially, but is limited to ~ 40% after 1 h of exposure. No additional mass
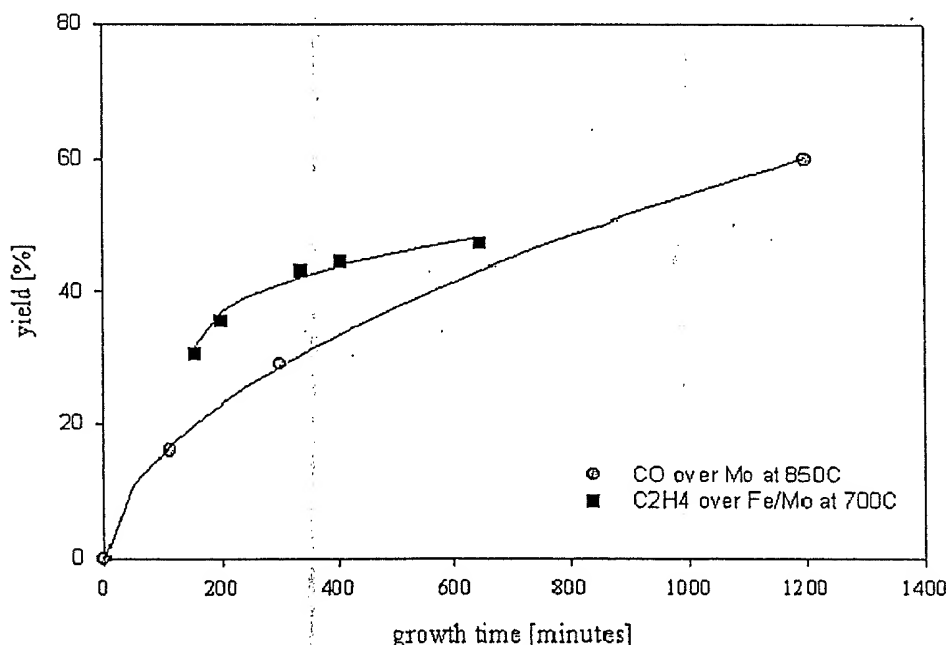

Fig. 2. Yield as a function of time for CO over Mo particles and C_2H_4 over Fe:Mo particles. The fits give a time dependence of $t^{0.5}$ and $t^{0.4}$, respectively.
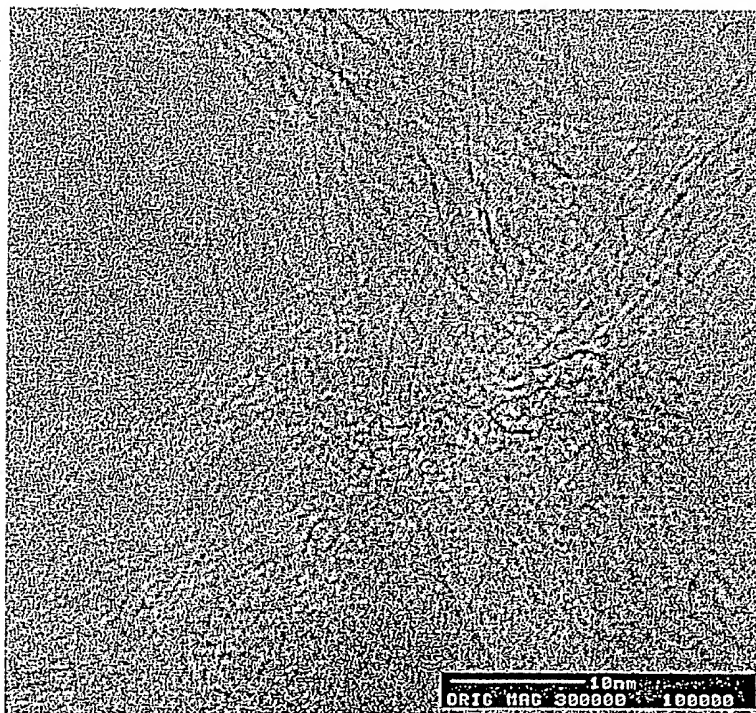
Fig. 3. TEM image of SWNT grown at 850°C by 1200 sccm CO over an alumina:Fe:Mo catalyst.

increase is observed even for much longer exposures (up to 20 h).

We have also grown SWNTs from C_2H_4 using this technique. The 90:9:1 alumina:Fe:Mo catalyst is first reduced by exposing to 1000 sccm Ar and 0.33 sccm H_2 at 800°C for 30 min. The growth reaction then proceeds at the reaction temperature by adding 0.66 sccm C_2H_4 to the gas flow. The resulting product is nanotube bundles containing SWNTs and DWNTs (Fig. 4). One hundred nanotube cross-sections were observed at several reaction temperatures to count the relative number of single- to double-walled nanotubes. The amount of DWNTs increases from 30% at 700°C to 70% at 850°C. Outer diameters of the individual tubes in a bundle range from 0.5 to 3 nm. There appears to be no correlation between outer diameter and number of walls, other than that the smallest nanotubes (< 1 nm diameter) are never double-walled.

The mass yield of nanotubes increases at a similar rate for reaction temperatures from 700 to 850°C, but the termination is temperature dependent. For reactions at 850°C, the yield increases until it reaches 7%, at which point the growth terminates. As the reaction temperature is lowered, the yield reaches higher levels before growth termination. At 700°C, the growth does not terminate, but its rate decreases as shown in Fig. 2.

4. Discussion

The most remarkable aspect of this series of experiments is that, in every case, only SWNTs and sometimes DWNTs are produced with diameters in the range 0.5–3 nm. We see no 5–20 nm diameter multiwalled nanotubes that are typically produced by supported catalyst particles. We believe that the key difference responsible for these effects is that we have arranged for the growth reaction rate to be limited by the supply of carbon to the catalyst particles, whereas the multiwalled nanotube growth is
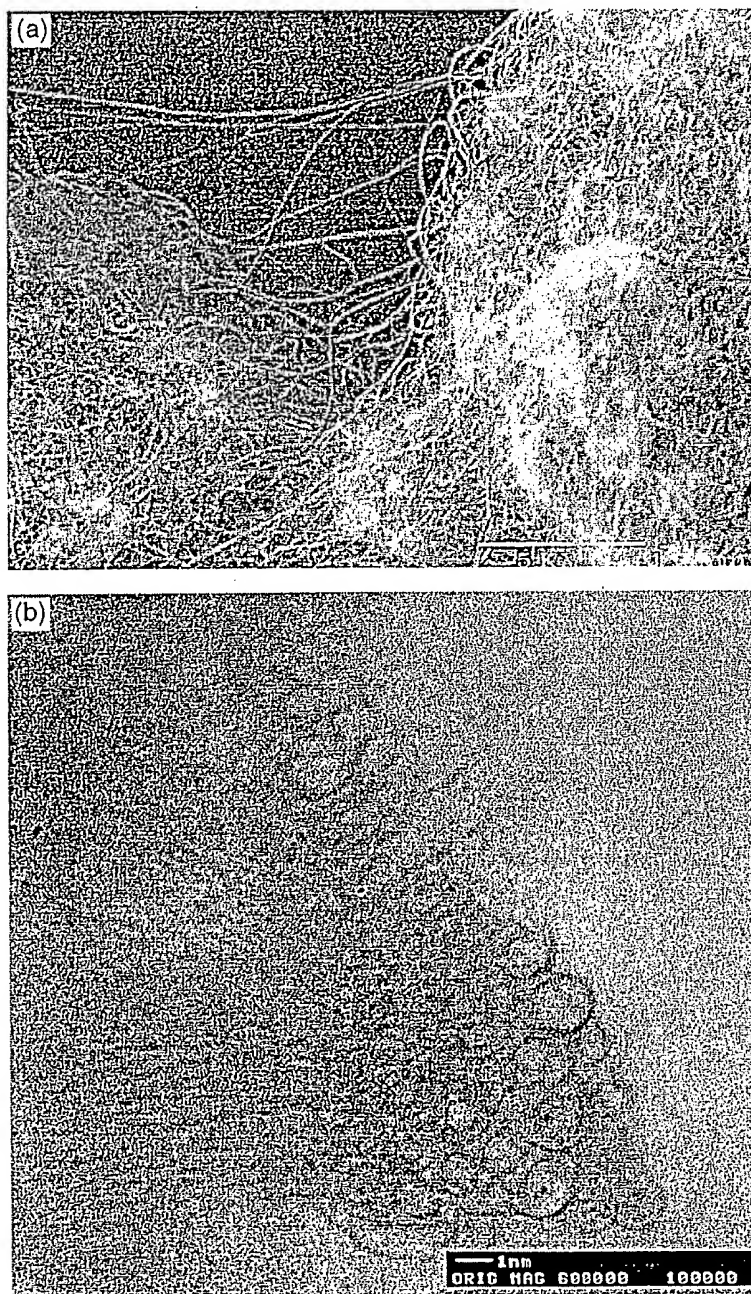
Fig. 4. (a) SEM image of nanotube ropes grown at 800°C in 1000 sccm Ar, 0.66 sccm C_2H_4, 0.33 sccm H_2, (b) TEM shows that the ropes consist of nanotubes of diameter 0.5–3 nm and 1 or 2 walls.

thought to be limited by the diffusion of carbon through the catalyst particles [9].

In the reaction of CO to produce nanotubes, the slow carbon supply rate arises because CO decomposition is a bimolecular disproportionation that involves the breaking of two strong CO triple bonds: such a reaction is expected to proceed very slowly except at very high pressures, much greater than our reaction pressure of ~ 1 atm. The catalytic decomposition of C_2H_4 proceeds quickly at 1 atm, so in this case we slow the reaction down by limiting the partial pressure of C_2H_4 to 0.5 Torr.

Evidence that we have successfully changed the rate-limiting step from carbon diffusion through the catalytic particle to carbon supply to the catalytic particle can be found in three aspects of the C_2H_4 system. First, it has been found that the product mass increase rate varies linearly with the C_2H_4 partial pressure. Second, ignoring termination, the mass growth rate is independent of the reaction temperature from 700 to 850°C. If the reaction were limited by diffusion of carbon through the metal, the rate would double from 700 to 850°C assuming an Arrhenius temperature dependence and the activation energy of carbon diffusion through iron [10]. Admittedly, the current experiments only measure a bulk growth rate as opposed to the microscopic growth rate of an individual nanotube. However, assuming that the same number of nanotubes nucleate per unit mass of catalyst, the two rates are proportional. Finally, we find that the bulk growth rate of carbon on the catalyst equals 5% of the mass of carbon in ethylene that flows over the catalyst. Although this is not 100% as would be expected of a supply limited reaction, a simple model assuming laminar flow suggests that only 5% of the ethylene molecules strike the catalyst bed.

Changing from a diffusion-limited to a supply-limited reaction by lowering the carbon supply to the catalyst reduces the carbon concentration in the catalyst particles as they form nanotubes. A lower carbon concentration will likely allow the structures to form more slowly, giving each carbon atom more time to anneal to its lowest energetic configuration. Therefore, the observed products should match those which are predicted to have the lowest energy.

We considered the energetics of structures that could grow off of the catalyst particles by calculating the energy per carbon atom as a function of structure size. For SWNTs, the caps were neglected in favor of the vastly greater number of carbon atoms in the side walls. The energies of carbon atoms at the nanotube–metal interface and nanotube ends were neglected since we are only considering the final product energies and not nucleation or growth mechanisms. We also considered a graphene capsule entirely surrounding the catalyst particle. For all catalyst particle diameters, one expects the graphene cylinder to be lower in energy than the capsule since the cylinder has only simple curvature compared with the complex curvature of the capsule. However, the attractive interaction between the graphene capsule and the metal particle will lower the energy per atom of the capsule. We used simple formulas for the energies of curved graphene sheets for the nanotubes [10] and large fullerenes for the capsules [11]. An estimate for the graphene–metal interaction was taken from an experimental measurement of the energy of the graphite–ferrite interface [12]. The result, displayed in Fig. 5, shows that the nanotube energy is lower than that of the capsule in a diameter range similar to the SWNT diameters we find in our experiments. These calculations lend support to our hypothesis that in our experiments supply-limited growth allows more time to anneal to the lowest-energy structure so that smaller particles produce nanotubes while larger particles are encapsulated. This model could give further insight into the presence or absence of DWNTs and multiwalled nanotubes if the relative graphene–graphene and graphene–metal interaction strengths were well known.

For experiments in which the reaction time is short, we have observed that the SWNTs grow with a particle at one end and closed at the other. This supports nucleation of these nanotubes by the yarmulke mechanism, described previously [8], in which a hemispherical graphene cap forms on the catalyst particles and lifts off to nucleate closed nanotubes.

As shown in Fig. 2, both CO disproportionation over Mo catalyst particles at 850°C and the reaction of C_2H_4 with Fe/Mo particles at 700°C appear to generate SWNTs that grow continuously without termination of the growth reaction. These results constitute the first demonstration of continuous generation of SWNTs with lengths that are, in principle,
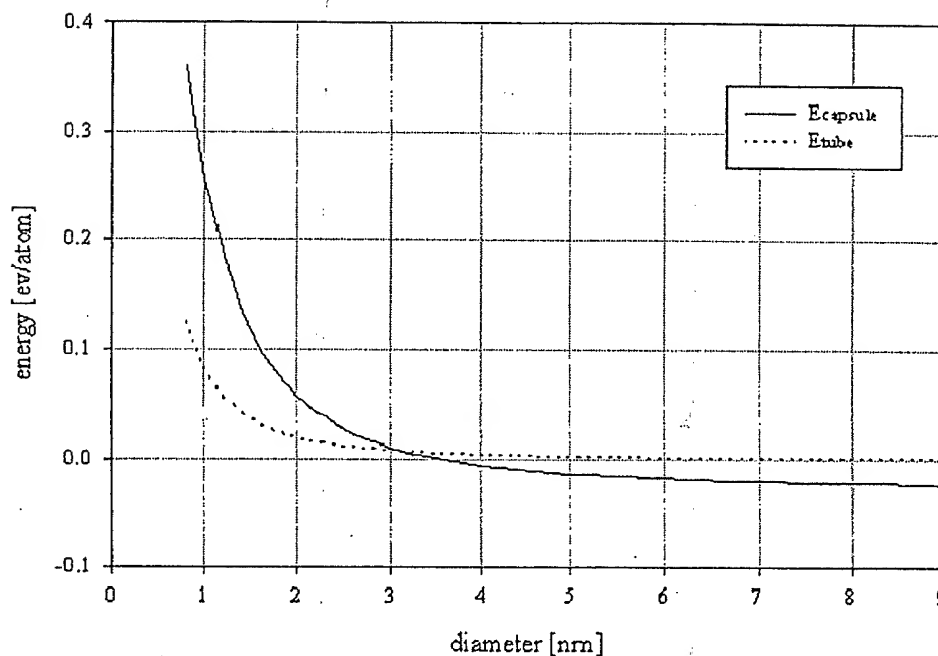
Fig. 5. Energies of capsules an single-wall nanotubes relative to an infinite graphene sheet.

arbitrarily long. In practice, however, the mass of the grown nanotubes exhibits a time dependence that is less than linear, so that growth slows more and more with increasing time (a fit of the data sets in Fig. 2 give roughly square root dependencies of yield on time). We attribute this slowing growth to the increasing diffusion time of the carbon feed-stock molecules through the thickening mat of nanotubes surrounding the catalyst particles.

The growth termination mechanism for the Fe/Mo catalyst at higher temperatures is not clear. One possibility is that a new graphene cap forms on the surface of a particle which has already nucleated a nanotube and encapsulates the particle, thus terminating the nanotube growth. That the termination is more effective at higher temperatures could be explained in terms of a higher carbon concentration in the particle at higher temperature leading to more frequent nucleation of a second graphene cap. This mechanism could also explain the presence of DWNTs. If the second cap forms on the catalytic particle inside the first nanotube, it could lift off to nucleate a second nanotube. As stated earlier, the proportion of DWNTs increases with temperature as well.

5. Conclusions

We have demonstrated the ability to grow nanotubes by catalytic decomposition of C_2H_4 and CO only from the small particles in a supported catalyst system, leading to the growth of SWNTs and deactivation of multiwalled nanotube growth by encapsulation of larger particles. For certain conditions, nanotubes can apparently be grown to arbitrary length, but become limited by the diffusion of reactants to the catalyst particles. This problem has been solved for the production of multiwalled nanotubes from this catalyst by using flat alumina flakes, as opposed to fumed alumina particles, so that the nanotubes grow aligned in large bundles, keeping their growing ends exposed to the gaseous feedstock. Similar modifications to the current technique may allow the bulk production of SWNTs.

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